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(54) CHEMICAL SYNTHESIS APPARATUS

(71) We, G. V. PLANER LIMITED, a British Company, of Windmill Road, Sunbury on Thames, Middlesex, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to chemical synthesis apparatus, known as metal atom solution reactor. It has particular, though not exclusive, application where metal atoms or other vapours produced at high temperatures, e.g. in the range 200°—4000°C and solutions of various compounds are used as reactants in formation of chemical products on a batch or a continuous basis.

Applications are *inter-alia* in the preparation of organo-metallic compounds, or organic polymers which contain metal atoms, of semi-conductor materials, of slurries of condensed metal vapours or metal oxide vapours in inert solvents, and catalyst support materials coated with condensed metal films.

Examples of such preparations occur in the condensation of the vapours of certain metals especially the transition metals of groups IV and VIII into solutions of organic compounds such as toluene, naphthalene or cyclo octa-1,5-diene. Many metal vapours after condensation act as catalyst precursors for the oligomerisation of organic compounds, (for example, butadiene), which is another type of application of the apparatus.

In accordance with the conventional designs of metal atom solution reactors, the reactor comprises a rotatable enclosure evacuable through one end via a rotary vacuum seal. The enclosure is cooled as required from the outside by contact with liquid or gaseous coolants. Reactions are carried out in the following way. The first chemical constituent, e.g. a metal vapour, is evaporated from an evaporation means which is mounted towards the centre of said rotatable evacuated enclosure, the enclosure is rotated during the reaction so that the vapour of the constituent condenses on the inside walls of the enclosure. The second chemical constituent is present in the enclosure as a pure liquid

or in a solution of low vapour pressure. Rotation of the enclosure spreads the constituent out in a thin layer on the inside walls of the enclosure and the first chemical constituent condenses into it.

Such reactors have two main limitations. They are not easily scaled-up in size and they are not easily made to operate continuously. Both limitations arise because the rotary vacuum seal becomes increasingly complex and costly as its size is increased which is a requirement when the size of the evaporation means is increased or if devices are to be fitted within the reactor for continuous feeding of the first and second constituents and for removal of reaction products.

Two alternative designs of reactors which partly overcome these limitations have been proposed hitherto.

In one form of continuous operation apparatus proposed, continuous replacement of the solution component is achieved by introducing the solution in the form of a spray directed towards the top of the inner walls of a stationary evacuable enclosure, which in this case takes the form of an upright cylinder, and allowing the liquid to drain down the walls of said enclosure during which time it may interact with metal or other vapour produced by evaporation means located centrally at the lower end of said evacuable enclosure. The solution drains into a trough from whence it is transferred by a pump or other means to a collector, or if insufficiently reacted, to the top of the enclosure where it is re-introduced for further reaction. In this system the rate of transfer of solution and of reaction is limited to that of a thin surface layer of solution falling freely under gravity over the inner walls of said enclosure and this sets a limit to the rate of reaction achievable in a given size enclosure.

In a further alternative design hitherto proposed, the reactor comprises a stationary evacuable enclosure inside which is set a rotatable centrifugal cylinder, mounted on a vertical axis with a rotary vacuum seal through the bottom of the enclosure. The first constituent is generated as a vapour

from a heating device near the centre of the rotating centrifugal cylinder and the vapour condenses on the walls of the cylinder. The second constituent in liquid or solution form is sucked from the surrounding stationary enclosure by centrifugal pump action to spin as a thin film moving upwards on the walls of the centrifugal cylinder and therefore relies on rotation of the walls at a comparatively high speed. After reaching the top of the walls of the cylinder it is returned to the stationary enclosure. Contact between the two constituents occurs on the walls of the centrifugal cylinder. The main weakness in this design is the need to have a rotary vacuum seal at the bottom of the enclosure, necessarily in contact with the liquid or solution in the enclosure. It is extremely difficult to operate such a seal if the temperature of the liquid or solution is less than -40°C , because of the limitations of elastomeric and lubricant materials. Thus, many important reactions involving metal atoms which require temperatures below -40°C cannot be attempted in this apparatus.

It is an object of the present invention to provide an improved chemical apparatus which overcomes the above problems.

In accordance with one aspect of the present invention, there is provided chemical synthesis apparatus comprising a stationary evacuable chamber acting as, or enclosing a reaction container, means mounting evaporation means for evaporating a first chemical constituent within said reaction container, means for introducing into said container a second chemical constituent in liquid or solution form, means for carrying said second chemical constituent from a lower level to the region above said evaporation means using a moveable member rotatable about an axis which is horizontal or at a small angle (up to 30°) below horizontal, means for agitating the surface of the film and means for removing the reaction product from said chamber.

Thus, on rotation through the lower portion of the reaction container (hereinafter referred to as the reservoir), the rotary member is partly immersed in, and is wetted by, a film of the solution or liquid which it carries as a continuously renewed film of the second constituent above the evaporation source. The shape of the rotary member can be the frustum of a sphere or ovoid or an open-ended cone but is preferably cylindrical.

The evaporation source is mounted within the hollow rotary member.

Improved mixing of the first and second constituents is obtained by means of a baffle(s), vane(s) or weir(s) fixed at one end outside the rotary member and in contact with the liquid film on the inside of the member. These ensure further agitation of

the solution thus presenting a larger area of the solution to the first chemical constituent. The baffle(s), vane(s) or weir(s) can also be arranged at an angle to the direction of the axis of motion of the moving member and thus confer lateral motion to the solution forcing the liquid to flow along the direction of the axis of rotation. The rotary member may comprise of gauze mesh, perforated metal or sheet metal. The cylindrical surface of the rotary member may be corrugated, ribbed or smooth and unbroken.

When the rotary member transfers a film of solution from the reservoir to the region above the evaporation source, solution on the outside of such rotary member can drip from, or be thrown off said member to be trapped by the cooled surface of the reaction container, whence it can drain back to the reservoir. In this way the excess solution on the outside of the rotary member is always retained within the cooled region of the evacuable enclosure, and thus its vapour pressure is maintained at the requisite low level. The reaction container can be of any shape but it should preferably conform to the shape of the rotary member, i.e. with a cylindrical rotary member a reaction container which is cylindrical or close to cylindrical is the preferred shape. It may have one or both ends open.

Where it is necessary to cool the solution to maintain the vapour pressure within the reactor at a sufficiently low level, say less than 10^{-2} mm of mercury a cool surface is provided within the enclosure and in contact with the reaction container which is kept cool by thermal conduction.

The evaporation means can be one or more of many types of source such as, but not exclusively, resistance heated electron beam heated, sputtering, magnetron sputtering etc. and such source or sources can comprise a continuous evaporant feed mechanism.

Chemical synthesis apparatus and method in accordance with the present invention, will now be described, by way of example, with reference to the accompanying drawings in which:

Fig. 1 is a schematic representation of one embodiment of the apparatus;

Fig. 2 is a schematic representation of a further embodiment of the apparatus;

Fig. 3 is schematic representation of parts of apparatus of other embodiments of the invention.

Referring to Fig. 1, an evacuable container 10 is connected by conduit 12 to conventional vacuum pumping equipment.

An evaporation source 14 comprises a filament 16 and crucible with evaporant charge 18.

The liquid reactant is introduced at one end of the container 10 via an inlet valve 20.

The reactant collects in the lower part of the evacuable chamber 10 which is cooled by flow of coolant through jacket 24. The reactant also enters the reaction container 26 which is cooled by being partially immersed in the solution in contact with cooling jacket 24. The rotary member 28 which is rotated from outside the chamber through a small rotary seal 30 lifts a film of liquid from the reservoir to the region above the evaporant source 14 where it reacts with the evaporant and is then returned to the reservoir from which it may be drained through drain valve 34 at the lowest point of the drainage channel 48. Coolant enters the jacket through inlet 36 and leaves at outlet 38.

The axle 32 is maintained horizontally or at a small angle preferably, but not exclusively, between 0—30° to the horizontal.

The rotary member 28 may consist of a hollow cylinder or frustum of gauze, perforated metal, or solid sheet. It is moved or rotated on its axle 32 via the rotary vacuum seal 30 at speeds adjustable up to several hundred revolutions per minute to ensure as great an effective surface of liquid is exposed to the metal atom flux as is practicable thus reducing risk of 'surface saturation'.

A sloping vane or weir 42 interrupts the steady film of solution on the inner surface of rotary member 28 and confers lateral motion to the solution so that the evaporant can interact with a fresh portion of the solution in each revolution.

Continuous flow or batch flow of the reactant is arranged as required between the solution inlet 20, over the inner surface of rotating member 28, where the reaction with the evaporant occurs, and out via the drain valve 34. Since the rotating member will be in close thermal contact with cooled surface of jacket 24 and can therefore contract, it is mounted on its spindle via a set of vanes 40 which can deflect slightly to take up differences in dimensions due to such contraction and thus ensure coaxial motion of the rotary member on its axle 32.

A large port 44 in wall of evacuable enclosure 10 allows access for insertion of any type of evaporation source and other appropriate mechanisms such as evaporant feed system 46.

Fig. 2 shows another embodiment of the invention in which the cooling jacket 24 is totally within the evacuable enclosure 10. An additional feature of this embodiment is that the inner surface 26 of the cooling jacket constitutes the reaction container. Solution is retained in the container by lips 50 and 52. Lip 52 is removable to enable rotary member 28 to be inserted into the reaction container. The charge 18 in the evaporation source is replenished by means of the wire feed 46.

Fig. 3 shows a cross section view of part of the reactor shown in Fig. 1, illustrating one

form of the rotary member 28 and agitation of the solution by the weir 42. The collecting channel 48 and the support vanes 40 are also shown in cross-section.

It will be appreciated that the reactant entering the evacuable chamber in any embodiment of the apparatus may be in the form of a liquid, a solution, or a suspension of finely divided solids in liquid, otherwise known as a slurry.

According to one example of the method of the present invention, bis-1-chloronaphthalenechromium, a compound useful as a hydrogenation catalyst and as a starting material for the preparation of other organometallic compounds of chromium with catalytic activity, via facile reactions with alkyl or aryl phosphines, phosphites or iso-cyanides is prepared in the following manner.

The evacuable enclosure is pumped to a pressure below 10^{-3} Torr. Calcium chloride brine (or other refrigerant), cooled by an external refrigerator to -18°C , is pumped through the cooling jacket around the reaction vessel. Liquid 1-chloronaphthalene is sucked into the reaction vessel. The liquid is carried round on the inside surface of the rotary member (e.g. a cylinder) in a film. The rotation speed is about 200 r.p.m. A sloping weir assists in exchange of liquid between that lying within the rotating cylinder and that outside the rotating part in the reaction container. Liquid spraying off the outer surface of the rotating cylinder is constrained by the wall of the reaction container and drains back to the lower part of said container. Evaporation of chromium from a resistively heated evaporation furnace is commenced. Under the prevailing low pressure ($<10^{-2}$ Torr during evaporation of chromium), the chromium atoms pass efficiently from the furnace to condense in the thin film of liquid being carried over by the rotating cylinder. The solid product, bis-1-chloronaphthalenechromium, is formed by reaction between the chromium atoms and 1-chloronaphthalene in the liquid phase. The product is only slightly soluble in the 1-chloronaphthalene, so that after a time the liquid contains a fine suspension of the solid product. Periodically, the outlet valve is opened to allow some of the liquid in the reaction vessel, comprising 1-chloronaphthalene plus dissolved or suspended product and small amounts of suspended solid chromium, to drain into a receiving vessel which has been evacuated. Additional 1-chloronaphthalene is added through the inlet tube to replenish that withdrawn. Additional granular chromium metal is added as required using an evaporation source feed mechanism.

The liquid withdrawn from the reaction vessel is worked-up by standard techniques. The 1-chloronaphthalene is stripped-off un-

der reduced pressure, the solid residue is extracted with diethyl ether, the solution filtered, and the filtrate evaporated to give pure bis-1-chloronaphthalenechromium in a yield of 70% based on the chromium evaporated.

WHAT WE CLAIM IS:—

1. Chemical synthesis apparatus comprising an evacuable chamber acting as or enclosing a stationary reaction container means mounting evaporation means for evaporating a first chemical constituent in said reaction container, means for introducing into said container a second chemical constituent in liquid or solution form, means for carrying said second chemical constituent from a lower level to the region above said evaporation means using a moveable member rotatable about an axis which is horizontal or at a small angle (up to 30°) below horizontal, means for agitating the surface of the film and means for removing the reaction product from said chamber.
2. Apparatus according to claim 1 wherein said container comprises a cooling jacket.
3. Apparatus according to claim 1 wherein part of said container constitutes a cooling jacket.
4. Apparatus according to any of claims 1, 2 or 3 wherein said movable member is in close proximity to part of the inside surface of said container.
5. Apparatus according to any of claims, 1, 2, 3 or 4, wherein said movable member comprises a surface of gauze mesh, perforated metal, or sheet metal.
6. Apparatus according to claim 5 where shape of movable member is cylindrical, the surface of a frustum, or part of the surface of a sphere or of an ovoid.
7. Apparatus according to any of claims 1, 2, 3 or 4, wherein said movable member has a corrugated or ribbed surface.
8. Apparatus according to any of claims 1, 2, 3 or 4, wherein said movable member comprises a series of vanes mounted on the periphery of a symmetrical surface.
9. Apparatus according to any of claims 5, 6 and 7, wherein a vane or weir is mounted inside and adjacent inner surface of said movable member.
10. Apparatus according to claim 9, wherein said vane or weir is arranged to interrupt the film of said second constituent on the inner surface of said movable member.
11. Apparatus according to claim 9 wherein said vane or weir is arranged to confer lateral motion of said second constituent over the inner surface of said movable member.
12. Apparatus according to any of the preceding claims in which said evaporation

means comprises a resistively heated member.

13. Apparatus according to any of claims 1 to 11 in which said evaporation means comprises an electron beam heated member.

14. Apparatus according to any of claims 1 to 11 in which said evaporation means comprises a sputtering source.

15. Apparatus according to any of claims 12, 13 and 14 wherein said evaporation means comprises a means for evaporant feed.

16. A method of chemical synthesis in which a first chemical constituent is produced from an evaporation source within a reaction container in an evacuable chamber, a second chemical constituent in liquid, solution or slurry form is introduced into the reaction container. The carriage of a film of second chemical constituent to the region above said evaporation source is effected by a moving member, and second constituent and or reaction product is removed from the system after circulation around the reaction region.

17. A method according to claim 16 wherein the second constituent is removed from the system and fresh second constituent added during the course of evaporation of the first constituent.

18. A method according to either of claims 16 or 17 wherein the reaction container is cooled.

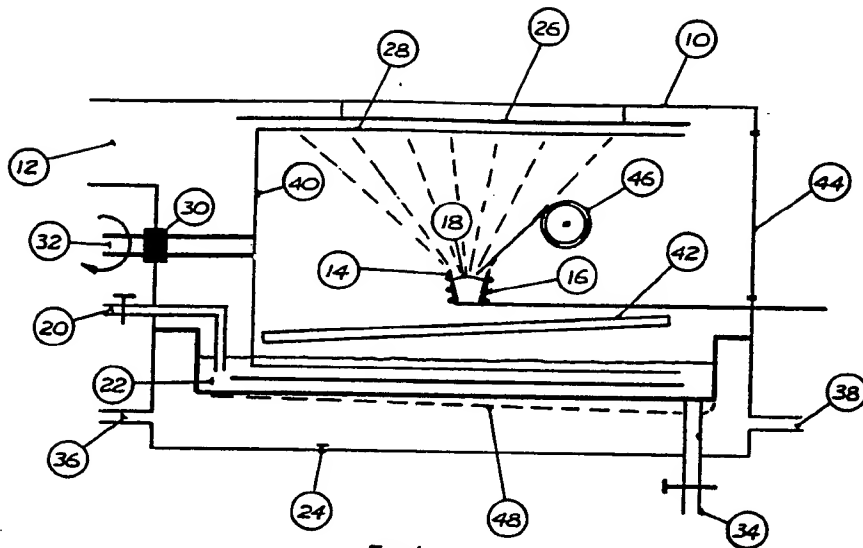
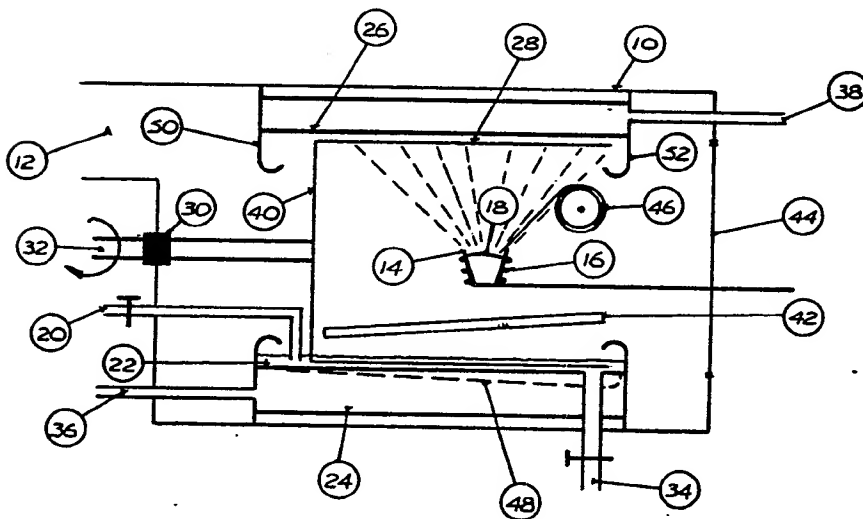
19. A method according to any of claims 16, 17 and 18 wherein surface of film of second chemical constituent is agitated by a vane or weir.

20. A method according to any of claims 16, 17, 18 and 19 wherein lateral motion is conferred on second chemical constituent relative to said moving member by a sloping vane or weir.

21. A method according to any of claims 16, 17, 18, 19 or 20 wherein the reaction product is removed after partial circulation around the reaction region.

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FIG. 1.FIG. 2.

